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EPA Office of Compliance Sector Notebook Project

Profile of the Organic Chemical Industry

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Office of Compliance
Office of Enforcement and Compliance Assurance
U.S. Environmental Protection Agency
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This report is one in a series of volumes published by the U.S. Environmental Protection Agency (EPA) to provide information of general interest regarding environmental issues associated with specific industrial sectors. The documents were developed under contract by Abt Associates (Cambridge, MA), and Booz-Allen & Hamilton, Inc. (McLean, VA). This publication may be **purchased** from the Superintendent of Documents, U.S. Government Printing Office. A listing of available Sector Notebooks and document numbers is included at the end of this document.

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Cover photograph by Steve Delaney, EPA. Photograph courtesy of Vista Chemicals, Baltimore, Maryland. Special thanks to Dave Mahler.

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EPA/310-R-95-017.	Stone, Clay, Glass and Concrete Ind.	Scott Throwe	564-7013
EPA/310-R-95-018.	Transportation Equip. Cleaning Ind.	Virginia Lathrop	564-7057

Industry Sector Notebook Contents: Organic Chemicals

Exhibits Index

List of Acronyms

AFS - AIRS Facility Subsystem (CAA database)
AIRS - Aerometric Information Retrieval System (CAA database)
BIFs - Boilers and Industrial Furnaces (RCRA)
BOD - Biochemical Oxygen Demand
CAA - Clean Air Act
CAAA - Clean Air Act Amendments of 1990
CERCLA - Comprehensive Environmental Response, Compensation and Liability Act
CERCLIS - CERCLA Information System
CFCs - Chlorofluorocarbons
CO - Carbon Monoxide
COD - Chemical Oxygen Demand
CSI - Common Sense Initiative
CWA - Clean Water Act
D&B - Dun and Bradstreet Marketing Index
ELP - Environmental Leadership Program
EPA - United States Environmental Protection Agency
EPCRA - Emergency Planning and Community Right-to-Know Act
FIFRA - Federal Insecticide, Fungicide, and Rodenticide Act
FINDS - Facility Indexing System
HAPs - Hazardous Air Pollutants (CAA)
HSDB - Hazardous Substances Data Bank
IDEA - Integrated Data for Enforcement Analysis
LDR - Land Disposal Restrictions (RCRA)
LEPCs - Local Emergency Planning Committees
MACT - Maximum Achievable Control Technology (CAA)
MCLGs - Maximum Contaminant Level Goals
MCLs - Maximum Contaminant Levels
MEK - Methyl Ethyl Ketone
MSDSs - Material Safety Data Sheets
NAAQS - National Ambient Air Quality Standards (CAA)
NAFTA - North American Free Trade Agreement
NCDB - National Compliance Database (for TSCA, FIFRA, EPCRA)
NCP - National Oil and Hazardous Substances Pollution Contingency Plan
NEIC - National Enforcement Investigation Center
NESHAP - National Emission Standards for Hazardous Air Pollutants
NO_2 - Nitrogen Dioxide
NOV - Notice of Violation
NO_x - Nitrogen Oxides
NPDES - National Pollution Discharge Elimination System (CWA)
NPL - National Priorities List
NRC - National Response Center

NSPS -	New Source Performance Standards (CAA)
OAR -	Office of Air and Radiation
OECA -	Office of Enforcement and Compliance Assurance
OPA -	Oil Pollution Act
OPPTS -	Office of Prevention, Pesticides, and Toxic Substances
OSHA -	Occupational Safety and Health Administration
OSW -	Office of Solid Waste
OSWER -	Office of Solid Waste and Emergency Response
OW -	Office of Water
P2 -	Pollution Prevention
PCS -	Permit Compliance System (CWA Database)
POTW -	Publicly Owned Treatments Works
RCRA -	Resource Conservation and Recovery Act
RCRIS -	RCRA Information System
SARA -	Superfund Amendments and Reauthorization Act
SDWA -	Safe Drinking Water Act
SEPs -	Supplementary Environmental Projects
SERCs -	State Emergency Response Commissions
SIC -	Standard Industrial Classification
SO_2 -	Sulfur Dioxide
SO_x -	Sulfur Oxides
TOC -	Total Organic Carbon
TRI -	Toxic Release Inventory
TRIS -	Toxic Release Inventory System
TCRIS -	Toxic Chemical Release Inventory System
TSCA -	Toxic Substances Control Act
TSS -	Total Suspended Solids
UIC -	Underground Injection Control (SDWA)
UST -	Underground Storage Tanks (RCRA)
VOCs -	Volatile Organic Compounds

Message from the Administrator

I. INTRODUCTION TO THE SECTOR NOTEBOOK PROJECT

I.A. Summary of the Sector Notebook Project

Environmental policies based upon comprehensive analysis of air, water and land pollution are an inevitable and logical supplement to traditional single-media approaches to environmental protection. Environmental regulatory agencies are beginning to embrace comprehensive, multi-statute solutions to facility permitting, enforcement and compliance assurance, education/ outreach, research, and regulatory development issues. The central concepts driving the new policy direction are that pollutant releases to each environmental medium (air, water and land) affect each other, and that environmental strategies must actively identify and address these inter-relationships by designing policies for the "whole" facility. One way to achieve a whole facility focus is to design environmental policies for similar industrial facilities. By doing so, environmental concerns that are common to the manufacturing of similar products can be addressed in a comprehensive manner. Recognition of the need to develop the industrial "sector based" approach within the EPA Office of Compliance led to the creation of this document. Many of those who reviewed this notebook are listed as contacts in Section IX and may be sources of additional information. The individuals and groups on this list do not necessarily concur with all statements within this notebook.

The Sector Notebook Project was initiated by the Office of Compliance within the Office of Enforcement and Compliance Assurance (OECA) to provide its staff and managers with summary information for eighteen specific industrial sectors. As other EPA offices, states, the regulated community, environmental groups, and the public became interested in this project, the scope of the original project was expanded. The ability to design comprehensive, common sense environmental protection measures for specific industries is dependent on knowledge of several inter-related topics. For the purposes of this project, the key elements chosen for inclusion are: general industry information (economic and geographic); a description of industrial processes; pollution outputs; pollution prevention opportunities; Federal statutory and regulatory framework; compliance history; and a description of partnerships that have been formed between regulatory agencies, the regulated community and the public.

For any given industry, each topic listed above could alone be the subject of a lengthy volume. However, in order to produce a manageable document, this project focuses on providing summary information for each topic. This format provides the reader with a synopsis of each issue, and references if more in-depth information is available. The contents of each profile were researched from a variety of sources, and were usually condensed from more detailed sources. This approach allowed for a wide coverage of activities that can be further explored based upon the citations and references listed at the end of this profile. As a check on the information included, each notebook went through an external review process. The Office of Compliance appreciates the efforts of all those that participated in this process which enabled us to develop more complete, accurate and up-to-date summaries.

I.B. Additional Information

Providing Comments

OECA's Office of Compliance plans to periodically review and update the notebooks and will make these updates available both in hard copy and electronically. If you have any comments on the existing notebook, or if you would like to provide additional information, please send a hard copy and computer disk to the EPA Office of Compliance, Sector Notebook Project, 401 M St., SW (2223-A), Washington, DC 20460. Comments can also be uploaded to the Enviroene Bulletin Board or the Enviroene World Wide Web for general access to all users of the system. Follow instructions in Appendix A for accessing these data systems. Once you have logged in, procedures for uploading text are available from the on-line Enviroene Help System.

Adapting Notebooks to Particular Needs

The scope of the existing notebooks reflect an approximation of the relative national occurrence of facility types that occur within each sector. In many instances, industries within specific geographic regions or states may have unique characteristics that are not fully captured in these profiles. For this reason, the Office of Compliance encourages state and local environmental agencies and other groups to supplement or re-package the information included in this notebook to include more specific industrial and regulatory information that may be available. Additionally, interested states may want to supplement the "Summary of Applicable Federal Statutes and Regulations" section with state and local requirements. Compliance or technical assistance providers may also want to develop the "Pollution Prevention" section in more detail. Please contact the appropriate specialist listed on the opening page of this notebook if your office is interested in assisting us in the further development of the information or policies addressed within this volume.

If you are interested in assisting in the development of new notebooks for sectors not covered in the original eighteen, please contact the Office of Compliance at 202-564-2395.

II. INTRODUCTION TO THE ORGANIC CHEMICALS INDUSTRY

This section provides background information on the size, geographic distribution, employment, production, sales, and economic condition of the organic chemical industry. The type of facilities described within the document are also described in terms of their Standard Industrial Classification (SIC) codes. Additionally, this section contains a list of the largest companies in terms of sales.

II.A. Introduction, Background, and Scope of the Notebook

The industrial organic chemical sector produces organic chemicals (those containing carbon) used as either chemical intermediates or end-products. This categorization corresponds to Standard Industrial Classification (SIC) code 286 established by the Bureau of Census to track the flow of goods and services within the economy. The 286 category includes gum and wood chemicals (SIC 2861), cyclic organic crudes and intermediates, organic dyes and pigments (SIC 2865), and industrial organic chemicals not elsewhere classified (SIC 2869). By this definition, the industry does not include plastics, drugs, soaps and detergents, agricultural chemicals or paints, and allied products which are typical end-products manufactured from industrial organic chemicals. In 1993, there were 987 establishments in SIC 286 of which the largest 53 firms (by employment) accounted for more than 50 percent of the industry's value of shipments. The SIC 286 may include a small number of integrated firms that are also engaged in petroleum refining and manufacturing of other types of chemicals at the same site although firms primarily engaged in manufacturing coal tar crudes or petroleum refining are classified elsewhere.[a]

The industrial organic chemical market has two broadly defined categories, commodity and specialty. Commodity chemical manufacturers compete on price and produce large volumes of small sets of chemicals using dedicated equipment with continuous and efficient processing. Specialty chemical manufacturers cater to custom markets, manufacture a diverse set of chemicals, use two or three different reaction steps to produce a product, tend to use batch processes, compete on technological expertise and have

[a] Variations in facility counts occur across data sources due to many factors including reporting and definitional differences. This notebook does not attempt to reconcile these differences, but rather reports the data as they are maintained by each source.

a greater value added to their products. Commodity chemical manufacturers have lower labor requirements per volume and require less professional labor per volume.

The *1992 Census of Manufactures for Industrial Organic Chemicals* reports employment of 124,800 and a 1992 value of shipments of $64.6 billion. This value of shipments does not include organic chemicals manufactured for captive use within a facility or the value of other non-industrial organic chemical products manufactured by the same facility. It does, however, include intra-company transfers which are significant in this industry. By comparison, the 1992 value of shipments for inorganic chemicals totaled $27.3 billion with employment of 103,400 people. The 1992 value of shipments for the entire chemical industry (SIC 28) was $292.3 billion and employment totaled 850,000. According to *Chemical and Engineering News*, the production of industrial organic chemicals has increased by three percent per year between 1983 and 1993 while employment has fallen by one percent per year over the same period indicating an overall increase in productivity for the sector. The same source reports the industry employed 153,000 people in 1993 while shipping products valued at $60.9 billion.

The Department of Commerce reported that output in the industrial organic chemical market grew five percent between 1992 and 1993 and is expected to continue to grow at the same rate partially on the strength of increased demand and production of methyl tert-butyl ether, a fuel oxygenate.

II.B. Characterization of the Organic Chemicals Industry

II.B.1. Industry size and geographic distribution

Industrial organic chemical facilities have an unusual distribution when compared to downstream manufacturing facilities. Most significantly, a small number of very large facilities account for the majority of the industry's value of shipments. The *1992 Census of Manufactures* (Exhibit 1) showed that only 113 of the 986 industrial organic chemical facilities (11 percent) had more than 250 employees. However, these facilities accounted for almost 70 percent of the value of shipments for the industry; the largest 16 plants (greater than 1,000 employees) accounted for about 25 percent of the total value of shipments.

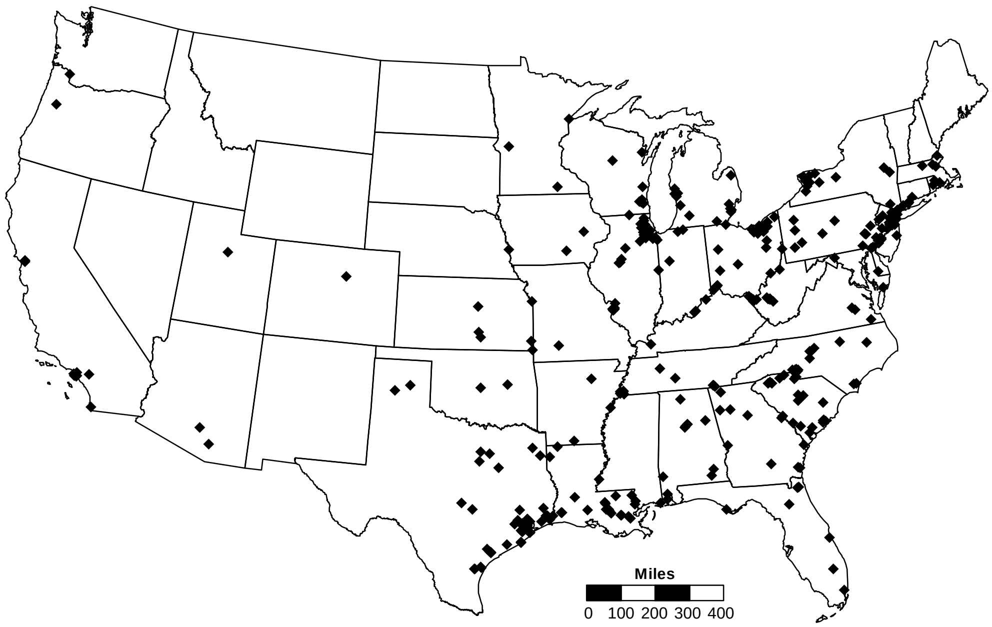
Exhibit 1: Small Number of Large Facilities Account for Majority of Shipments

Number of Employees	Number of Facilities	Percent of Facilities	Percent of Shipment Value
fewer than 10	259	26%	1%
10 to 49	301	30%	5%
50 to 249	313	32%	27%
250 to 499	60	6%	16%
500 to 999	37	4%	26%
1,000 or more	16	2%	25%
Total	986	100%	100%

Source: *1992 Census of Manufactures*

The industrial organic chemical sector is geographically diverse (Exhibit 2). Gum and wood chemical manufacture (SIC 2861) is concentrated in Missouri, Florida and Virginia. Cyclic crudes and intermediates (SIC 2865) and unclassified industrial organic chemicals (SIC 2869) are concentrated in Texas, Louisiana, New Jersey, Ohio, Illinois and West Virginia. Facility sites are typically chosen for their access to raw materials (petroleum and coal products for SICs 2865 and 2869 and wood for SIC 2861) and to transportation routes. In addition, because much of the market for industrial organic chemicals is the chemical industry, facilities tend to cluster near such end-users.

Exhibit 2: Organic Chemical Manufacturing Facilities (SIC 286)



(Source: U.S. EPA, Toxics Release Inventory Database, 1993)

Ward's Business Directory of U.S. Private and Public Companies, produced by Gale Research Inc., compiles financial data on U.S. companies including those operating within the organic chemical industry. Ward's ranks U.S. companies, whether they are a parent company, subsidiary or division, by sales volume within their assigned 4-digit SIC code. Readers should note that: (1) companies are assigned a 4-digit SIC that most closely resembles their principal industry; and (2) sales figures include total company sales, including subsidiaries and operations (not related to organic chemicals). Additional sources of company specific financial information include Standard & Poor's *Stock Report Services*, Dun & Bradstreet's *Million Dollar Directory*, Moody's Manuals, and annual reports.

Exhibit 3: Top U.S. Companies with Organic Chemical Operations		
Rank[a]	**Company**[b]	**1993 Sales** (millions of dollars)
1	Exxon Corp., Exxon Chemical Co. - S. Darien, CT	9,591
2	Dow Chemical USA - Midland, MI	9,000
3	Miles, Inc. - Pittsburgh, PA	5,130
4	Union Carbide Corp. - Danbury, CT	4,877
5	Amoco Chemical Co. - Chicago, IL	4,031
6	Chevron Chemical Co. - San Ramon, CA	3,354
7	Quantum Chemical Corp. - New York, NY	2,532
8	Witco Corp. - New York, NY	1,631
9	Ethyl Corp. - Baton Rouge, LA	1,600
10	Texaco Chemical Co. - Houston, TX	1,600

Note: [a] When Ward's Business Directory lists both a parent and subsidiary in the top ten, only the parent company is presented above to avoid double counting. Not all sales can be attributed to the companies' organic chemical operations.
[b] Companies shown listed SIC 286 as primary activity.

Source: Ward's Business Directory of U.S. Private and Public Companies - 1993.

II.B.2. Product Characterization

The two-digit SIC code 28, Chemicals and Allied Products, includes facilities classified as industrial organic chemical manufacturers under the three-digit SIC code 286. This includes gum and wood chemicals, cyclic crudes and intermediates and industrial organic chemical not elsewhere classified. The last category is by far the largest and most diverse of the three; however, its size distribution and industry structure are similar to those of the cyclic crudes and intermediates because both use primarily petroleum and coal derived feedstocks. In addition to industrial organic chemicals, seven separate types of product establishments are identified under Chemicals and Allied Products (SIC 28). Many of the other industry sectors within the two-digit SIC code 28, such as plastics materials and synthetics (SIC 282), are downstream users of the products manufactured by the industrial organic chemical industry. Others, such as the inorganic chemical sector, utilize unrelated feedstocks. The following list includes industrial organic chemicals (italicized) as well as other chemicals and allied product SIC codes included within SIC code 28.

SIC	Industry Sector	SIC	Industry Sector
281	Inorganic Chemicals	*2861*	*Gum and Wood Chemicals*
282	Plastics Materials and Synthetics	*2865*	*Cyclic Organic Chemicals*
283	Drugs	*2869*	*Industrial Organic Chemicals, n.e.c.*
284	Soaps, Cleaners, and Toilet Goods	287	Agricultural Chemicals
285	Paints and Allied Products	289	Miscellaneous Chemical Products

The industrial organic chemical industry uses feedstocks derived from petroleum and natural gas (about 90 percent) and from recovered coal tar condensates generated by coke production (about 10 percent). The chemical industry produces raw materials and intermediates, as well as a wide variety of finished products for industry, business and individual consumers. The important classes of products within SIC code 2861 are hardwood and softwood distillation products, wood and gum naval stores, charcoal, natural dyestuffs, and natural tanning materials.

The important classes of products within SIC code 2865 are: (1) derivatives of benzene, toluene, naphthalene, anthracene, pyridene, carbazole, and other cyclic chemical products, (2) synthetic organic dyes, (3) synthetic organic pigments, (4) cyclic (coal tar) crudes, such as light oils and light oil products; coal tar acids; and products of medium and heavy oil such as creosote oil, naphthalene, anthracene and their high homologues.

Important classes of chemicals produced by organic chemical industry facilities within SIC code 2869 include: (1) non-cyclic organic chemicals such as acetic, chloroacetic, adipic, formic, oxalic acids and their metallic salts, chloral, formaldehyde, and methylamine; (2) solvents such as amyl, butyl and ethyl alcohols; methanol; amyl, butyl, and ethyl acetates; ethyl ether, ethylene glycol ether and diethylene glycol ether; acetone, carbon disulfide, and chlorinated solvents such as carbon tetrachloride, tetrachloroethene, and trichloroethene; (3) polyhydric alcohols such as ethylene glycol, sorbitol, pentaerythritol, and synthetic glycerin; (4) synthetic perfumes and flavoring materials such as coumarin, methyl salicylate, saccharin, citral, citronellal, synthetic geraniol, ionone, terpineol, and synthetic vanillin; (5) rubber processing chemicals such as accelerators and antioxidants, both cyclic and acyclic; (6) plasticizers, both cyclic and acyclic, such as esters of phosphoric acid, phthalic anhydride, adipic acid, lauric acid, oleic acid, sebacic acid, and stearic acid; (7) synthetic tanning agents such as sulfonic acid condensates; and (8) esters and amines of polyhydric alcohols and fatty and other acids.

II.B.3. Economic trends

With organic chemicals as the single largest segment of chemical exports (accounting for nearly one-half of total chemical shipments to foreign markets), the industrial organic sector faces a market similar to the petrochemical industry. While the U.S. production is expected to continue to grow at two to four percent annually, there is increasing competition in the export market despite growing demand. World petrochemical demand is projected to increase from 320 million metric tons in 1992 to 575 million metric tons in 2010. The share accounted for by the United States, Western Europe and Japan is expected to drop from 71 to 63 percent. Products from the Gulf Cooperation Council and Pacific Rim countries, including China and Korea, will begin to compete with U.S. products in current export markets as new facilities are brought on-line. The U.S. is expected to maintain a positive trade balance in organic chemicals. Chemical imports of organic chemicals (some representing intra-company transfers) have been steady over the last five years. The reduced trade barriers due to the North American Free Trade Agreement (NAFTA) and the Uruguay Round of the General Agreement on Tariffs and Trade (GATT) have increased competition. Firms are adapting to the increased competition by emphasizing specialty chemicals and higher value-added products.

III. INDUSTRIAL PROCESS DESCRIPTION

This section describes the major industrial processes within the organic chemical industry, including the materials and equipment used, and the processes employed. The section is designed for those interested in gaining a general understanding of the industry, and for those interested in the inter-relationship between the industrial process and the topics described in subsequent sections of this profile -- pollutant outputs, pollution prevention opportunities, and Federal regulations. This section does not attempt to replicate published engineering information that is available for this industry. Refer to Section IX for a list of reference documents that are available.

This section specifically contains a description of commonly used production processes, associated raw materials, the by-products produced or released, and the materials either recycled or transferred off-site. This discussion, coupled with schematic drawings of the identified processes, provides a concise description of where wastes may be produced in the process. This section also describes the potential fate (via air, water, and soil pathways) of these waste products.

III.A. Industrial Processes in the Organic Chemicals Industry

Industrial Organic Chemicals - Overview

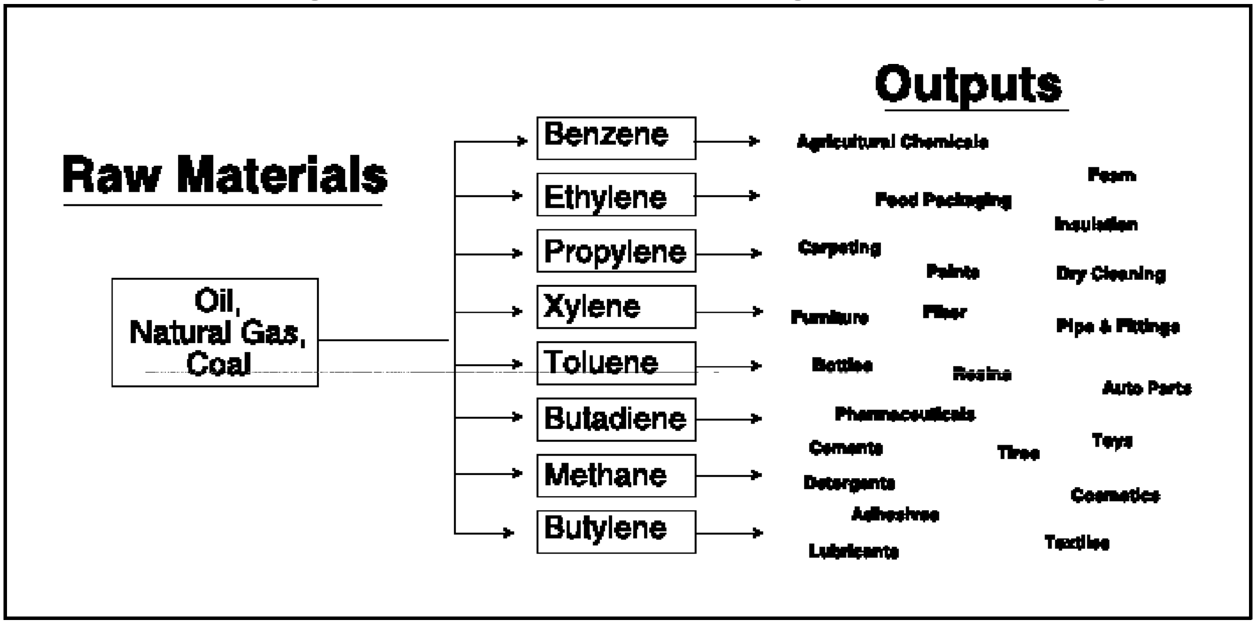
The industrial organic chemical sector includes thousands of chemicals and hundreds of processes. In general, a set of building blocks (feedstocks) is combined in a series of reaction steps to produce both intermediates and end-products. The chart and flow diagram below (Exhibits 4 and 5) show the primary organic chemical building blocks (generated principally from petroleum refining), a key subset of the large volume secondary building blocks and a set of large volume tertiary building blocks. The subsequent chart (Exhibit 6) shows the reaction types used to manufacture a sample of organic chemicals, and illustrates the large variety of processes used by the industry.

Exhibit 4: High Volume Organic Chemical Building Blocks

Primary Building Block	**Secondary Building Block**	**Tertiary Building Block**
Ethylene	Ethylene dichloride Ethylene oxide Ethylbenzene	Vinyl chloride Ethylene glycol Vinyl acetate
Propylene	Propylene oxide Acrylonitrile Isopropyl alcohol	 Acetone
Benzene	Ethylbenzene Cumene Cyclohexane	Styrene Phenol Acetone Adipic acid
Methanol	Acetic acid Formaldehyde Methyl t-butyl ether	Vinyl acetate
Toluene		
Xylenes p-isomer	 Terephthalic acid	
Butadiene		
Butylene		

Source: Szmant, *Organic Building Blocks of the Chemical Industry*

Exhibit 5: Organic Chemicals and Building Blocks Flow Diagram



The typical chemical synthesis process involves combining multiple feedstocks in a series of unit operations. The first unit operation is a chemical reaction. Commodity chemicals tend to be synthesized in a continuous reactor while specialty chemicals usually are produced in batches. Most reactions take place at high temperatures, involve metal catalysts, and include one or two additional reaction components. The yield of the reaction will partially determine the kind and quantity of by-products and releases. Many specialty chemicals require a series of two or three reaction steps. Once the reaction is complete, the desired product must be separated from the by-products by a second unit operation. A number of separation techniques such as settling, distillation or refrigeration may be used. The final product may be further processed, by spray drying or pelletizing for example, to produce the saleable item. Frequently by-products are also sold and their value may alter the process economics.

Exhibit 6: Reaction/Process Types by Chemical Category for a Sampling of Organic Chemicals

Generic Process	Ethers		Halocarbons			Hydrocarbons					Ketones	Nitrile
	Bis-1,2-Chloroisopropyl Ether	Ethylene Glycol Monomethyl Ether	Epichlorohydrin	Methyl Bromide	1,1,1-Trichloroethane	Butadiene	Hexane	Isoamylene	Styrene	Xylenes	Acetone	Acetonitrile
Alkoxylation		●										
Condensation	●											
Halogenation			●		●							
Oxidation												
Polymerization												
Hydrolysis												
Hydrogenation												
Esterification												
Pyrolysis								●		●	●	
Alkylation									●			
Dehydrogenation						●			●			
Amination												
Nitration												
Sulfonation												
Ammoxidation												●
Carbonylation												
Hydrohalogenation				●								
Dehydration												
Dehydrohalogenation			●									
Oxyhalogenation					●							
Catalytic Cracking							●					
Hydrodealkylation										●		
Phosgenation												
Extraction						●		●				
Distillation						●		●				
Other											●	
Hydration												

Exhibit 6 (cont.): Reaction/Process Types by Chemical Category for a Sampling of Organic Chemicals

Generic Process	Nitro-Carbon	Phenol	Salt	Misc.		Acid	Alcohols		Alde-hyde	Amine	Amide	Anhy-drides	Ester
	Nitrobenzene	p-Aminophenol	Sodium Benzoate	Dichlorodiphenyl Sulfone	Methylene Diphenyl Diisocyanate	Sulfonic Acid	n-Butanol	1,6-Hexanediol	Benzaldehyde	Hydroxylamine	Formamide	Tetrachloroprophthalic Anhydride	Dimethyl Terephthalate
Alkoxylation													
Condensation					●								
Halogenation												●	
Oxidation			●					●	●			●	●
Polymerization													
Hydrolysis										●			
Hydrogenation		●					●	●					
Esterification								●					●
Pyrolysis													
Alkylation													
Dehydrogenation													
Amination (Ammonolysis)											●		
Nitration	●												
Sulfonation				●									
Ammoxidation													
Carbonylation						●			●				
Hydrohalogenation													
Dehydration												●	
Dehydrohalogenation													
Oxyhalogenation													
Catalytic Cracking													
Hydrodealkylation													
Phosgenation					●								
Extraction													
Distillation													
Other			●	●									
Hydration							●						

Source: U.S. Development Document for Effluent Limitations, Guidelines and Standards for the Organic Chemicals, Plastics and Synthetic Fibers Point Source Category

The separation technology employed depends on many factors including the phases of the substances being separated, the number of components in the mixture, and whether recovery of by-products is important. Numerous techniques such as distillation, extraction, filtration, and settling can be used singly or in combination to accomplish separations and are summarized in publications such as *Perry's Chemical Engineers' Handbook* or basic texts on chemical plant design.

Relatively few organic chemical manufacturing facilities are single product/process plants. Additionally, many process units are designed so that production levels of related products can be varied over wide ranges. This flexibility is required to accommodate variations in feedstock and product prices which can change the production rate and processes used, even on a short-term (less than a year) basis. A 1983 survey showed that 59 percent of industrial organic plants had more than one product or process and that seven percent had more than 20 (USEPA Development Document for Effluent Limitations Guidelines and Standards for the Organic Chemicals, Plastics and Synthetic Fibers Point Source Category).

The type of reaction process used to manufacture chemicals depends on the intended product; however, several types of reactions are common: polymerization, oxidation, and addition. Polymerization is a chemical reaction usually carried out with a catalyst, heat or light (often under high pressure) in which a large number of relatively simple molecules combine to form a chain-like macromolecule. Oxidation, in the strict sense, means combining oxygen chemically with another substance although this name is also applied to reactions where electrons are transferred. Addition covers a wide range of reactions where a double or triple bond is broken and a component added to the structure. Alkylation can be considered an addition, as can some oxidation reactions. The following charts list the reactions used to produce a subset of organic chemical products.

Four Specific Industrial Organic Chemicals

This profile examines the reactions of four high-volume chemicals (ethylene, propylene, benzene and vinyl chloride) chosen to illustrate the use of typical chemical feedstocks based on several factors, including the quantity of chemical produced, and the health and environmental impacts of the chemical. Ethylene, propylene, and benzene are all primary building blocks and their reaction products are used to produce still other chemicals. Vinyl chloride is an important tertiary building block.

The four chemicals described below illustrate several key points. First, primary building blocks are typically used in more reactions than the building blocks further down the chain. Second, most feedstocks can participate in more than one reaction and third, there is typically more than one reaction route to an end-product. The end-products of all of these chemicals can be used in numerous commercial applications; *Riegel's Handbook of Industrial Chemistry,* listed in the reference section, describes many uses.

Ethylene

The major uses for ethylene are in the synthesis of polymers (polyethylene) and in ethylene dichloride, a precursor to vinyl chloride. Other important products are ethylene oxide (a precursor to ethylene glycol) and ethylbenzene (a precursor to styrene). While ethylene itself is not generally considered a health threat, several of its derivatives, such as ethylene oxide and vinyl chloride, have been shown to cause cancer. The distribution of uses is shown below.

The manufacturing processes that use ethylene as a feedstock are summarized in the table below along with reaction conditions and components. In 1993, 18.8 million metric tons of ethylene were produced in the United States making ethylene the fourth largest production volume organic chemical in the United States. Ethylene dichloride, ethylbenzene, and ethylene oxide (products of ethylene reactions) are all among the top 50 high production volume organic chemicals in the United States (*Chemical and Engineering News*).

Exhibit 7: Distribution of Uses for Ethylene

Product	**Percent of Ethylene Use**
Polyethylene	54
Ethylene dichloride	16
Ethylbenzene-styrene	7
Ethylene oxide-glycol	13
Ethanol	1
Linear olefins-alcohol	3
Vinyl acetate	2
Other	4

Source: *Kirk-Othmer Encyclopedia of Chemical Technology*

Exhibit 8: Manufacturing Processes Using Ethylene

Process	Target Product	Process Conditions: Pressure (MPa)	Process Conditions: Temperature (ºC)	Process Conditions: Catalyst	Reaction Components	Other Characteristics
Polymerization	Low Density Polyethylene (LDPE)	60 - 350	350		Oxygen or Peroxide	
	High Density Polyethylene	0.1 - 20	50 - 300	Molybdenum Chromium oxide		
	Polyethylene	Low		Aluminum alkyls Titanium oxide		
Oxidation	Ethylene Oxide	1 - 2	250 - 300	Silver	1,2-Dichloro-ethane, Oxygen	60% is converted to ethylene glycol using an acid catalyst
	Acetaldehyde	0.3	120 - 130	Copper chloride/ palladium chloride	Oxygen	Vapor phase
	Vinyl acetate	0.4 - 1	170 - 200	Palladium	Acetic acid	
<u>Addition</u> Halogenation\ hydrohalogenation	Ethylene dichloride		60	Iron, aluminum, copper, or antimony chlorides	Chlorine	Feedstock for vinyl chloride and trichloroethylene and tetrachloroethylene
	Ethyl chloride	0.3 - 0.5		Aluminum or iron chlorides	HCl	Precursor of styrene
Alkylation	Ethylbenzene			Aluminum, iron, and boron chlorides	Benzene	
Hydroformation	Propionaldehyde	4 - 35	60 - 200	Cobalt	Synthesis gas (carbon monoxide and hydrogen)	

Source: *Kirk-Othmer Encyclopedia of Chemical Technology*

Propylene

Over half of the U.S. propylene supplies (10.2 million metric tons produced in 1993) are used in the production of chemicals. The primary products are polypropylene, acrylonitrile, propylene oxide, and isopropyl alcohol. Of these, propylene, acrylonitrile and propylene oxide are among the top fifty high-volume chemicals produced in the United States. Acrylonitrile and propylene oxide have both been shown to cause cancer, while propylene itself is not generally considered a health threat. The table below shows the use distribution of propylene.

Exhibit 9: Distribution of Propylene Use

Product	**Percent of Propylene Use**
Polypropylene	36
Acrylonitrile	16
Propylene oxide	11
Cumene	9
Butyraldehydes	7
Oligomers	6
Isopropyl alcohol	6
Other	9

Source: Szmant, *Organic Building Blocks of the Chemical Industry*

The important propylene reactions are shown below. The products of the reactions are the feedstocks for numerous additional products.

Exhibit 10: Manufacturing Processes Using Propylene

Process	Target Product	Process Conditions			Reaction Components	Other Characteristics
		Pressure (MPa)	Temperature	Catalyst		
Polymerization	Polypropylene			Aluminum alkyls/Titanium oxide		
Oxidation	Acrylonitrile		400	Phosphomolybdate	Ammonia Oxygen	Commercially valuable by-products are acetonitrile and hydrogen cyanide
	Propylene oxide				Oxygen Ethylbenzene	Commercially valuable by-product is *tert*-butyl alcohol
Addition Chlorohydrination	Propylene oxide	25	37	Tungsten	Hypochlorous acid	
Hydrolysis	Isopropyl alcohol		267		Water	

Source: *Kirk-Othmer Encyclopedia of Chemical Technology*

Benzene

Benzene is an important intermediate in the manufacture of industrial chemicals and over 5.5 million metric tons were produced in the U.S. in 1993 (*Chemical and Engineering News*). Over 95 percent of U.S. consumption of benzene is for the preparation of ethylbenzene, cumene, cyclohexane, nitrobenzene, and various chlorobenzenes as shown in the table below.

Exhibit 11: Distribution of Benzene Use

Product	Percent of Benzene Use
Ethylbenzene	52
Cumene	22
Cyclohexane	14
Nitrobenzene	5
Chlorobenzenes	2
Linear detergent alkylate	2
Other	3

Source: *Kirk-Othmer Encyclopedia of Chemical Technology*

The following table summarizes the primary benzene reactions. The products are frequently feedstocks in the synthesis of additional chemicals. Benzene is considered a human carcinogen by the Agency.

Exhibit 12: Manufacturing Processes Using Benzene

Process	Target product	Process Conditions: Pressure (MPa)	Process Conditions: Temperature (°C)	Process Conditions: Catalyst	Reaction components	Other characteristics
Oxidation	Phenol	0.6	90-100		Cumene, Oxygen	Most important phenol synthesis
	Maleic anhydride	0.1-0.2	350-400	Vanadium oxide	Butane Oxygen	
	Styrene	0.1	580-590	Iron oxide	Ethylene benzene	
Addition Alkylation	Ethylbenzene	0.2-0.4	125-140	Aluminum chloride	Benzene, Ethylene	Precursor to styrene
	Ethylbenzene	2.0	420-430	Zeolite	Benzene, Ethylene	Precursor to styrene
	Cumene	0.3-1.0	250-350	Phosphoric acid/silicate	Benzene, Propylene	
	2,6-Xylenol	0.1-0.2	300-400	Aluminum oxide	Phenol, Methanol	
Hydrogenation	Cyclohexanone	0.1	140-170	Palladium	Phenol, Hydrogen	
	Cyclohexanol	1.0-2.0	120-200	Nickel/silicon oxide and aluminum oxide	Phenol Hydrogen	
	Cyclohexane	2.0-5.0	150-200	Nickel	Benzene, Hydrogen	
	Aniline	.18	270	Copper	Nitrobenzene, Hydrogen	
Nitration	Nitrobenzene	0.1	60		Benzene, sulfuric acid, nitric acid	
Sulfonation	Surfactants	0.1	40-50		Alkylbenezenes/ Sulfur trioxide	
Chlorination	Chlorobenzene	0.1	30-40	Aluminum chloride/ Iron chloride	Benzene, Chlorine	
Condensation	Biphenol A	0.1	50-90	HCl	Phenol, Acetone	

Source: *Franck and Stadelhofer, "Industrial Aromatic Chemistry"*

Vinyl Chloride

Vinyl chloride is one of the largest commodity chemicals in the U.S. with over 6.25 million metric tons produced in 1993. It is also considered a human carcinogen by the EPA. Vinyl chloride polymers are the primary end use but various vinyl ethers, esters, and halogen products can also be made as shown in the table below.

Exhibit 13: Manufacturing Processes Using Vinyl Chloride

Process	Target Product	Process Conditions			Reaction components	Other characteristics
		Pressure (MPa)	Temperature (°C)	Catalyst		
Polymerization	Polyvinylchloride		50	Peroxides		
Substitution at the Carbon-Chlorine Bond	Vinyl acetates, alcholates, vinyl esters and vinyl ethers			Palladium	Alkyl halides	
Addition	Various halogen addition products					

Source: *Kirk-Othmer Encyclopedia of Chemical Technology*

III.B. Raw Material Inputs and Pollution Outputs

Industrial organic chemical manufacturers use and generate both large numbers and quantities of chemicals. The industry emits chemicals to all media including air (through both fugitive and direct emissions), water (direct discharge and runoff) and land. The types of pollutants a single facility will release depend on the feedstocks, processes, equipment in use and maintenance practices. These can vary from hour to hour and can also vary with the part of the process that is underway. For example, for batch reactions in a closed vessel, the chemicals are more likely to be emitted at the beginning and end of a reaction step (associated with vessel loading and product transfer operations), than during the reaction. The potential sources of pollutant outputs by media are shown below.

Exhibit 14: Potential Releases During Organic Chemical Manufacturing

Media	Potential Sources of Emissions
Air	Point source emissions: stack, vent (e.g. laboratory hood, distillation unit, reactor, storage tank vent), material loading/unloading operations (including rail cars, tank trucks, and marine vessels) Fugitive emissions: pumps, valves, flanges, sample collection, mechanical seals, relief devices, tanks Secondary emissions: waste and wastewater treatment units, cooling tower, process sewer, sump, spill/leak areas
Liquid wastes (Organic or Aqueous)	Equipment wash solvent/water, lab samples, surplus chemicals, product washes/purifications, seal flushes, scrubber blowdown, cooling water, steam jets, vacuum pumps, leaks, spills, spent/used solvents, housekeeping (pad washdown), waste oils/lubricants from maintenance
Solid Wastes	Spent catalysts, spent filters, sludges, wastewater treatment biological sludge, contaminated soil, old equipment/insulation, packaging material, reaction by-products, spent carbon/resins, drying aids
Ground Water Contamination	Unlined ditches, process trenches, sumps, pumps/valves/fittings, wastewater treatment ponds, product storage areas, tanks and tank farms, aboveground and underground piping, loading/unloading areas/racks, manufacturing maintenance facilities

Source: *Designing Pollution Prevention into the Process- Research, Development and Engineering*

III.C. Management of Chemicals in the Production Process

The Pollution Prevention Act of 1990 (PPA) requires facilities to report information about the management of TRI chemicals in waste and efforts made to eliminate or reduce those quantities. These data have been collected annually in Section 8 of the TRI reporting Form R beginning with the 1991 reporting year. The data summarized below cover the years 1992 through 1995 and are meant to provide a basic understanding of the quantities of waste handled by the industry, the methods typically used to manage this waste, and recent trends in these methods. TRI waste management data can be used to assess trends in source reduction within individual industries and facilities, and for specific TRI chemicals. This information could then be used as a tool in identifying opportunities for pollution prevention compliance assistance activities.

From the yearly data presented below it is apparent that the portion of TRI wastes reported as recycled on-site has remained reasonably constant between 1992 and 1995 (projected). While the quantities reported for 1992 and 1993 are estimates of quantities already managed, the quantities reported for 1994 and 1995 are projections only. The PPA requires these projections to encourage facilities to consider future waste generation and source reduction of those quantities as well as movement up the waste management hierarchy. Future-year estimates are not commitments that facilities reporting under TRI are required to meet.

Exhibit 15 shows that the organic chemical industry managed about 6.3 trillion pounds of production-related waste (total quantity of TRI chemicals in the waste from routine production operations) in 1993 (column B). Column C reveals that of this production-related waste, seven percent was either transferred off-site or released to the environment. Column C is calculated by dividing the total TRI transfers and releases by the total quantity of production-related waste. In other words, about 90 percent of the industry's TRI wastes were managed on-site through recycling, energy recovery, or treatment as shown in columns E, F and G, respectively. The majority of waste that is released or transferred off-site can be divided into portions that are recycled off-site, recovered for energy off-site, or treated off-site as shown in columns H, I and J, respectively. The remaining portion of the production related wastes (three percent), shown in column D, is either released to the environment through direct discharges to air, land, water, and underground injection, or it is disposed off-site.

Exhibit 15: Source Reduction and Recycling Activity for the Organic Chemical Industry (SIC 286) as Reported within TRI

A	B	C	D	On-Site			Off-Site		
				E	F	G	H	I	J
Year	Quantity of Production-Related Waste (10^6 lbs.)[a]	% Released and Transferred[b]	% Released and Disposed[c] Off-site	% Recycled	% Energy Recovery	% Treated	% Recycled	% Energy Recovery	% Treated
1992	6,313	7%	3%	71%	7%	15%	2%	1%	2%
1993	6,325	7%	3%	71%	7%	15%	2%	1%	1%
1994	6,712	---	2%	71%	8%	15%	2%	1%	1%
1995	6,645	---	2%	72%	7%	15%	2%	1%	<1%

[a] Within this industry sector, non-production related waste < 1% of production related wastes for 1993.
[b] Total TRI transfers and releases as reported in Section 5 and 6 of Form R as a percentage of production related wastes.
[c] Percentage of production related waste released to the environment and transferred off-site for disposal.